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# A modified cooperative model of relaxation and aging kinetics 

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Received 16 March 1992


#### Abstract

This paper describes the properties of a kinetic formula derived from a differential equation based on a time-domain induction mechanism reminiscent of that encountered in Bose-Einstein statistics, $\mathrm{d}(\dot{n} / n) / \mathrm{d} t=-a \dot{n} / n+\beta(\dot{n} / n)^{2}$, with $n$ denoting the relaxing quantity and $\dot{n}$ its time derivative. While, as shown earlier, the corresponding equation without the normalization of $\dot{n}$ with regard to $n$ produced an exponential relation between $\dot{n}$ and $n$, a generalized power law is obtained in the present case. As in the former case the distribution of relaxation times is discrete, the spectral lines being integer-valued fractions of a fundamental time constant.


## 1. Introduction

This paper is part of a series of communications exploring the potential of kinetic formulae based on the time-domain version of a Bose-Einstein (BE) distribution. After a brief review of the properties of a direct equivalent of a BE formula, yielding the rate of change of the relaxing quantity as a function of time, we present a modified equation, where the rate is normalized with regard to the number of flow entities yet to undergo transition to the relaxed state. It will be demonstrated that, while the first formula yields a so-called exponential law (or logarithmic time law), the second one yields a power law often found in experiments. Before proceeding, some limiting types of transient flow in solids, such as primary creep, stress relaxation and physical aging, will be briefly defined. With regard to the concept of 'flow units' as normally done, we assume the macroscopic process to consist of a number of transitions of such units from the initial to the relaxed state, without specifying their exact character.

Formally, when interpreted in spectral terms, transient flow in solids is characterized by relatively broad distributions of relaxation times, $\tau$. Often a box-type distribution of $\log \tau$ provides a fair description of experimental facts. In essence, this amounts to saying that the quantity in question varies linearly with log time, $t$, this being referred to as the logarithmic time law [1]. Apart from using a box-type $\tau$ spectrum, one obtains the $\log t$ law starting from an exponential relation between the rate of change of the quantity being measured and the quantity itself.

For stress relaxation, for instance, one arrives at the relation [1]

$$
\begin{equation*}
\dot{\sigma}=-A \exp \left(v \sigma / k_{\mathrm{B}} T\right) \tag{1}
\end{equation*}
$$

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with $\sigma$ denoting the stress, $\dot{\sigma}=\mathrm{d} \sigma / \mathrm{d} t, v$ a volume (of activation), $k_{\mathrm{B}} T$ the thermal energy and $A$ a constant. This equation has the obvious physical appeal of being directly obtainable from the Boltzmann factor, assuming that the energy of activation of the flow units involved in the process decreases with the energy stored locally due to the applied stress. In order to achieve $\dot{\sigma} \rightarrow 0$ for $\sigma \rightarrow 0$, one has to consider flow in the opposite direction. This yields a $\sinh (v \sigma / k T)$ dependence, which, for all practical purposes, can be approximated by equation (1), however.

Apart from the above equation, expressing the idea of stress-dependent thermal activation (SDTA), and the concept of relaxation-time spectra (RTS), the so-called stretched exponential (Kohlrausch-Williams-Watts or Kww function)

$$
\begin{equation*}
\sigma=\sigma_{0} \exp \left[-(t / \tau)^{\alpha}\right] \tag{2}
\end{equation*}
$$

has been used frequently to describe the kinetics of fiow, dielectric response, aging, etc [2,3]. Again, equation (2) describes a process extending over a broader time range than that which would correspond to an unmodified exponential, provided that $\alpha<1$. It may be noted that a physically plausible derivation of equation (2) is associated with major difficulties [4].

An important quantity characterizing a relaxation process is the slope of the inflection region defined as $F=-(\mathrm{d} \sigma / \mathrm{d} \ln t)_{\max }$. A straight line through the inflection point cuts the $\sigma(t=0)$ and $\sigma(t \rightarrow \infty)$ lines at $t_{0}$ and $t_{1}$, respectively, as shown in figure 1 . The straight-line approximation of the process leads to

$$
\begin{equation*}
\sigma_{0}-\sigma_{\infty}=F \ln \left(t_{1} / t_{0}\right) \tag{3}
\end{equation*}
$$

where $\sigma_{0}$ has been corrected with regard to $\sigma_{\infty}$, i.e. the stress remaining when $t \rightarrow \infty$.

It has been amply demonstrated that for solids of various structure and composition

$$
\begin{equation*}
F=(0.1 \pm 0.01)\left(\sigma_{0}-\sigma_{\infty}\right) \tag{4}
\end{equation*}
$$

showing that the extension of the stress relaxation curves in the straight-line approximation is about four decades (4.3) of time [1]. Similar values have been reported for primary creep and physical aging of polymers [2]. In both cases, equation (4) applies at temperatures that are not too close to a thermal transition region [1]. Translated to the KWW function, equation (4) implies $\alpha \simeq 0.27(=\mathrm{e} / 10)$, which is close to the values of about $1 / 3$ to $1 / 4$ found experimentally [2]. We mention the general validity of equation (4) in order to support the notion that the kinetics of the processes in question are largely independent of structural details of the solid under study [5]. Projected $c$.to the SDTA theory, equation (4) yields $v=10 k_{\mathrm{B}} T / \sigma_{0}$, which certainly contradicts the numerous attempts in the past to correlate the activation volume with specific structural features. For details of the topics discussed above the reader is referred to a review published earlier [1].

## 2. The Bose-Einstein-like cooperative model

It is generally accepted that interactions between the elementary flow units and their transitions to the relaxed state play an important role in the present context [5].

However, there are considerable difficulties associated with a proper theoretical description of such a situation, especially since the nature of the elementary processes and the structural units they involve are not known. A simple model making use of a mechanism similar to that underlying Bose-Einstein (BE) statistics has been shown earlier to reproduce the basic features of relaxation processes in solids $[6-8]$ as depicted by the SDTA approach. The essence of the method is the replacement of $\exp (-k t)$ by

$$
\begin{equation*}
\dot{\sigma}=-k F /\left(A \mathrm{e}^{k t}-1\right) \tag{5}
\end{equation*}
$$

which is equivalent to

$$
\begin{equation*}
\dot{\sigma}=-k F\left(\mathrm{e}^{\sigma / F}-1\right) . \tag{6}
\end{equation*}
$$

Here $F$ is the slope of the inflection region, as given above, $k$ denotes the inverse of the relaxation time $\tau$, and $A=1+\epsilon$, with $\epsilon \ll 1$. Under certain simplifying conditions integration of equation (5) yields

$$
\begin{equation*}
\sigma=\sigma_{0}-F \ln \left[1-\left(\dot{\sigma}_{0} / k F\right)\left(1-\mathrm{e}^{-k t}\right)\right] . \tag{7}
\end{equation*}
$$

We note that this model produces the same exponential $\dot{\sigma}(\sigma)$ dependence as the SDTA concept. In addition, the difficulty of applying the exponential $\dot{\sigma}(\sigma)$ variation according to SDTA to the well documented linear scaling with regard to $\sigma_{0}=\sigma(t=0)$ is avoided here [1]. For $k t \ll 1$, we obtain the logarithmic time law. Details of this approach can be found in $[6-8]$. It is to be emphasized that the BE type modification of the usual $\exp (-t / \tau)$ exponential uses the concept of a single relaxation time in its original intent.

A distinct advantage of using a formula such as equation (5) is the simplicity of the underlying cooperative mechanism, especially when considering the differential equation from which equation (5) can be obtained [11].

$$
\begin{equation*}
\ddot{n}=-a \dot{n}+b \dot{n}^{2}=-a \dot{n}[1-(b / a) \dot{n}] . \tag{8}
\end{equation*}
$$

Here, $n, \dot{n}$ and $\ddot{n}$ denote the relaxing quantity (number of unrelaxed entities constituting the macroscopic process) and its first and second time derivatives. Equation (8) depicts a global induction mechanism fitting the picture of a consolidating dense structure naturally. Contrary to the features of common interacting systems such as, for instance, the Ising lattice [9], the factor determining the rate is not the number of unrelaxed units. Instead, the induction factor is a linear function of the rate itself. From a physical point of view it is natural to imagine that the movement of a structural unit facilitates simultaneous movement of other units in its vicinity. The cooperative mechanism is thus restricted to the time interval being considered. The concept of free volume [2] and its central role in processes of the type under discussion may provide a physically tangible illustration.

The induction mechanism inherent in the concept of BE-like statistics, implying that the probability of a unit's transition to the unrelaxed state is linearly dependent on the number of other transitions taking place simultaneously, certainly has an element of physical appeal. In spite of this, its potential has not been appreciated by workers active in this field, who seem to favour physically elusive notions like that of the Kww function mentioned above.

The potential of the BE-like mechanism discussed in earlier papers [6-8] is not, as it may seem, exhausted by the shift from $\exp (-k t)$ to equation (5). The reason is that the differential equation yielding this shift can be modified in a number of ways. In the next section, we discuss the properties of the solutions of equation (8) in which the rate $\dot{n}$ has been replaced by the rate density $\dot{n} / n$ relative to the number of unrelaxed entities. It will be shown that a generalized power-law type $\dot{n}(n)$ relation emerges from such a modification. As is well known, the power law is extensively used as a method of describing flow kinetics in solids [1]. In polyethylene, for instance, the initial part of the stress relaxation process appears to follow an exponential $\dot{\sigma}(\sigma)$ relation, while a power law fits the final stage [10].

## 3. Modified cooperative model

We now consider the following modification of the basic differential equation (8),

$$
\begin{equation*}
\ddot{n}=-a \dot{n}+(\beta+1) \dot{n}^{2} / n=-a \dot{n}(1-[(\beta+1) / a] \dot{n} / n) \tag{9}
\end{equation*}
$$

where $\beta$ is a constant, and where the induction term does not comprise $\dot{n}$ but the ratio $\dot{n} / n$, that is the rate density with regard to the number of unrelaxed units, $n$. An obvious advantage of using $\dot{n} / n$ is the scale invariance of the resulting equations. Equation (9) is identical with

$$
\begin{equation*}
\mathrm{d}(\dot{n} / n) / \mathrm{d} t=-a \dot{n} / n+\beta(\dot{n} / n)^{2} \tag{10}
\end{equation*}
$$

which provides an even simpler picture of the underlying induction mechanism.
Equations (9) and (10) can be integrated to provide relations between the quantities $\dot{n}, n$ and $t$. Owing to the similarity of equations (8) and (10) we obtain for $\dot{n}(t)$

$$
\begin{equation*}
\dot{n}=-a n /\left[\beta\left(B \mathrm{e}^{a t}-1\right)\right] \tag{11}
\end{equation*}
$$

with $B=\left(1-a n_{0} / \beta \dot{n}_{0}\right)$. Normally $-a n_{0} / \beta \dot{n}_{0} \ll 1$. In the following, the notation $B=1+\epsilon$ will be used. For $t \rightarrow \infty$, the rate $\dot{n}$ (negative) falls to zero. Integration of equation (11) gives for $n(t)$,

$$
\begin{equation*}
n(t)=n_{0}\left[(B-1) /\left(B-\mathrm{e}^{-a t}\right)\right]^{1 / \beta} \tag{12}
\end{equation*}
$$

This equation also defines the quantity $n_{\infty}$, i.e. the number of unrelaxed units as $t \rightarrow \infty$,

$$
\begin{equation*}
n_{\infty} / n_{0}=[(B-1) / B]^{1 / \beta} \tag{13}
\end{equation*}
$$

As can be seen, $n_{\infty}$ disappears only for $B=1$, implying $a n_{0} / \beta \dot{n}_{0} \rightarrow 0$. On the other hand, equation (11) for $\dot{n}(t)$ then becomes divergent. In principle, $n_{\infty}$ can be kept at negligible levels for $B$ sufficiently close to 1 .

A distinctive property of equations (9) and (10) is the power-law dependence of $\dot{n}$ on $n$, as expressed by the relation

$$
\begin{equation*}
\dot{n} / n=a / \beta+\left(\dot{n}_{0} / n_{0}-a / \beta\right)\left(n / n_{0}\right)^{\beta} \tag{14}
\end{equation*}
$$

This relation can be recast in the form

$$
\begin{equation*}
\dot{n}=(a / \beta) n\left[1-\left(n / n_{\infty}\right)^{\beta}\right] \tag{15}
\end{equation*}
$$

showing that $\dot{n}$ approaches zero for $n \rightarrow n_{\infty}$. The power-law character of $\dot{n}(n)$ is also evident from

$$
\begin{equation*}
n=n_{0}\left(n / n_{0}\right)^{\beta+1} \mathrm{e}^{-a t} \tag{16}
\end{equation*}
$$

### 3.1. The shape of the $n(\log t)$ curves

In this section we analyse the main parameters determining the slope of the $n(\log t)$ curves and their position along the log time axis. As already mentioned, equation (12) yields relaxation curves with finite values of $n_{\infty}$, cf equation (13). The magnitude of $n_{\infty}$ can be brought down to arbitrarily low levels by letting $B \rightarrow 1$. However, the $n_{\infty}$ value is coupled to the position of the $n(\ln t)$ curves along $\ln t$. Decreasing $\epsilon$ in $B=1+\epsilon$ implies a shift of the inflection region of the curves towards shorter times.

When characterizing the shape and position of the $n(\ln t)$ curves, the following parameters are of special interest: the slope $F$ of the inflection region (point) of such curves, and the two intercepts of a straight line tangent to the inflection with $n_{0}$ and $n_{\infty}$. These latter two quantities are denoted $t_{0}$ and $t_{1}$, respectively. Since in the present case $n_{\infty}$ may assume values different from zero, we also have to consider the corresponding intercept with $n=0$, denoted $t_{1}^{\prime}$. These definitions are clarified in figure 1.


Figure 1. Relaxation curves plotted as $n / n_{0}$ versus $\ln (a t)$ for $\beta=2$ and varying $\epsilon(=$ $B-1$ ): (a) $\epsilon=10^{-8}$, (b) $10^{-5}$, (c) $10^{-3}$, (d) 0.1 and (e) 1.0. The corresponding $\ln \left(t_{1} / t_{0}\right)$ ratios are: $5.196,5.180,5.037$, 3.997 and 3.102 , respectively.

The equations defining the slope $F$ and the intercepts $t_{0}, t_{1}$ and $t_{1}^{\prime}$ cannot be related to the parameters $a$ and $\beta$ of equation (10) in an explicit form. This applies also to the parameter $B(=1+\epsilon)$ entering the integrated equations (11) and (12). However, for $B$ and $\beta$ values that lead to $n(\ln t)$ curve shapes consistent with experimental facts, the errors incurred in the following approximations are practically negligible.

Let us denote the time at the inflection point by $t_{\mathrm{i}}$ and introduce the variable $x=a t_{\mathrm{i}}$. The value of $a t_{\mathrm{j}}$ is then calculated from the equation

$$
\begin{equation*}
x / \beta+1=B(1-x) \mathrm{e}^{x} \tag{17}
\end{equation*}
$$

giving

$$
\begin{equation*}
\ln \left(a t_{\mathrm{i}}\right) \simeq \ln \epsilon+\ln \beta-\epsilon\left(\beta^{2} / 2-1\right) \tag{18}
\end{equation*}
$$

where, for not too high values of $\beta$, the last term on the right-hand side can be neglected, resulting in the following approximate relation

$$
\begin{equation*}
a t_{\mathrm{i}} \simeq \epsilon \beta . \tag{19}
\end{equation*}
$$

A straight line tangent to the inflection point of $n(\ln t)$ produces the intercepts $t_{0}$ and $t_{1}$ with the $\ln t$ axis at $n_{0}$ and $n_{\infty}$, respectively. Omitting calculational details we show only the final expressions for $t_{0}$ and $t_{1}$ :

$$
\begin{equation*}
\ln \left(a t_{0}\right) \simeq \ln (\epsilon \beta)+(1+\beta)\left[1-(1+\beta)^{1 / \beta}\right] \tag{20}
\end{equation*}
$$

and

$$
\begin{equation*}
\ln \left(a t_{1}\right) \simeq \ln (\epsilon \beta)+(1+\beta)\left\{1-\{\epsilon(1+\beta)]^{1 / \beta}\right\} . \tag{21}
\end{equation*}
$$

The extension of the $n(\ln t)$ curves along the $\ln t$ axis expressed in terms of the straight line approximation is then found to be

$$
\begin{equation*}
\ln \left(t_{1} / t_{0}\right) \simeq(1+\beta)^{1+1 / \beta}\left(1-\epsilon^{1 / \beta}\right) . \tag{22}
\end{equation*}
$$

The first term on the right-hand side defines the inflection slope, the second is a correction factor reducing the value of $\ln \left(t_{1} / t_{0}\right)$ due to a finite $n_{\infty}$ level. As evident from equation (13),

$$
n_{\infty} / n_{0} \approx \epsilon^{1 / \beta}
$$

for sufficiently small $\epsilon$, i.e. $\epsilon \ll 1$.


Figure 2. Relaxation curves plotted as $n / n_{0}$ versus $\ln (a t)$ for $\beta=6$ and varying $\epsilon$ : (a) $\epsilon=10^{-14}$, (b) $10^{-10}$, (c) $10^{-6}$, (d) $10^{-2}$ and (e) 1.0. The $\ln \left(t_{1} / t_{0}\right)$ ratios are: 9.61 , $9.47,8.71,5.34$ and 3.03 , respectively.

The parameter $F / n_{0}$, central in this context with regard to its experimental background, cf equation (4), is given by

$$
\begin{equation*}
F / n_{0} \simeq(1+\beta)^{-(1+1 / \beta)} \tag{24}
\end{equation*}
$$

an expression independent of $n_{\infty}$. Relating $F$ instead to $n_{0}-n_{\infty}$ one obtains

$$
\begin{equation*}
F /\left(n_{0}-n_{\infty}\right) \simeq(1+\beta)^{-(1+1 / \beta)}\left(1-\epsilon^{1 / \beta}\right)^{-1} . \tag{25}
\end{equation*}
$$

Referring to the experimental fact that $F /\left(\sigma_{0}-\sigma_{\infty}\right) \simeq 0.1$, equation (4), we find from equation (24) that

$$
\begin{equation*}
\beta \simeq 6 \tag{26}
\end{equation*}
$$



Figure 3. Relaxation curves plotted as $n / n_{0}$ versus $\ln (a t)$ for $\beta=12$ and varying $\epsilon$ : (a) $\epsilon=10^{-14}$, (b) $10^{-9}$ and (c) $10^{-6}$. The $\ln \left(t_{1} / t_{0}\right)$ ratios are: 15.00, 13.24 and 11.01, respectively.

Here we have to note that the truncation of the $n(\ln t)$ curves as reflected by the $\epsilon$-containing term in equation (25) does not appear to represent a physical situation. When comparing equation (4) with the above results, we thus have to consider $n_{0}$ as the equivalent of $\sigma-\sigma_{\infty}$.

Although it is possible to work with both a negative and a positive sign in front of the rate constant $a$ in equation (10), we have limited the above discussion to the former case, since this produces $n(\ln t)$ curves falling monotonically with time, while the other alternative gives curves with two inflections.

The above conclusions pertaining to the shape of the $n(\ln t)$ curves are supplemented in graphical form in figures $1-3$, showing the course of $n(\ln t)$, normalized with regard to $n_{0}$, for different values of $\beta$ and $\epsilon$. As can be seen, the slope of the curves is determined by $\beta$ only, provided that $\epsilon$ is sufficiently small. The $n_{\infty}$ level evident from figures 1-3 depends strongly on $\epsilon$, at least for the $\beta$ values chosen here. Also, for very small $\epsilon$ the $n_{\infty} / n_{0}$ level may reach significant values since it is given by the $1 / \beta$ power of $\epsilon$, cf equation (23). The normalized slope $F / n_{0}$ depends only on $\beta$, while $F$ normalized with regard to $n_{0}-n_{\infty}$ depends on the $n_{\infty}$ level and, consequently, on $\epsilon$.

A particular feature of the diagrams of figures 1-3 is a tail at long times, reminiscent of corresponding curves based on a power law or a stretched exponential, as discussed below. Depending on the values of the parameters $\beta$ and $\epsilon$, this tail may be more or less pronounced. This also affects the extension of the rectilinear $n(\ln t)$ portion, corresponding to the exponential law, equation (6).

Another graphical supplement is figure 4 , showing the variation of $\ln \left(t_{1} / t_{0}\right)$ with $\beta$ for several $\epsilon\left(=-a n_{0} / \beta \dot{n}_{0}\right)$ values. As in figures $1-3$ above, $t_{1}$ relates to $n_{\infty}$, which makes $\ln \left(t_{1} / t_{0}\right)$ dependent on $\epsilon$. The same applies to $F /\left(n_{0}-n_{\infty}\right)$, while $F / n_{0}$ or $\ln \left(t_{1} / t_{0}\right)$ are largely independent of $\epsilon$, provided that its values are sufficiently small. Figure 4 shows that the experimentally verified ratio $F / n_{0} \simeq 0.1$, equation (4), requires $\beta \simeq 6$ ( $n_{\infty}$ assumed to be negligible). In fact, this $\beta$ value gives $F / n_{0}=0.103$, cf equation (24).

In order to attain a given value of $\ln \left(t_{1} / t_{0}\right), t_{1}$ relating to $n_{\infty}, \epsilon$ has to be sufficiently small. For instance, $\ln \left(t / t_{0}\right)=10$ cannot be attained for $\epsilon=B-1=$ $10^{-4}$ even when the range of $\beta$ values is extended to 100 , since the corresponding curve in figure 4 levels off asymptotically. For finite values of $n_{\infty}$ the value of $\beta$ corresponding to a given logarithmic ratio of $t_{1} / t_{0}$ as given, for instance, by



Figure 4. The variation of the ratio $\ln \left(t_{1} / t_{0}\right)$ with $\beta$ for different values of $\epsilon$ : (top to bottom) $\epsilon=10^{-14}, 10^{-12}, 10^{-10}$, $10^{-8}, 10^{-6}$ and $10^{-4}$.

Figure 5. The variation of $\ln \left(t_{1} / t_{0}\right)$ with $\beta$ for an extended range of $\beta$ values; $\epsilon$ as in figure 4.
equation (22), depends on $\epsilon$. This is illustrated in figure 5 where the $\beta$ range has been significantly extended.

The $\ln \left(t_{1} / t_{0}\right)$ versus $\beta$ data reproduced in figures 4 and 5 are the results of exact computer calculations. Compared with this, the approximation (22) above is highly accurate, since no difference between the two sets of results can be found within the range covered in the above illustrations.

### 3.2. Spectral properties of $n(t)$ and $\dot{n}(t)$

Relaxation processes are often described in terms of a spectrum of relaxation times, starting from the notion of a linear superposition of time exponentials. In the continuous case, the spectrum is obtained as the inverse Laplace transform of the relaxation function [1].

In a previous paper [11] elucidating the properties of the relaxation function based on equation (8), we demonstrated that the corresponding spectral distribution of $\tau$ is discrete for both $n(t)$ and $\dot{n}(t)$. In the present case, when basing the calculations on the modified equation (10), the structure of the $\tau$ spectrum is similar.

Also, in this case, the $n(t)$ and $\dot{n}(t)$ functions can be expressed in a unique way


Figure 6. Discrete distribution of relaxation times for $n(t) ; \epsilon=10^{-10}, \beta=6$; cf equation (29).


Figure 7. Discrete distribution of relaxation times for $n(t) ; \epsilon=10^{-2}, \beta=6$; cf equation (29).
as sums of exponentials, i.e.

$$
\begin{equation*}
n=n_{\infty}+\left(n_{0}-n_{\infty}\right) \sum_{k=1}^{\infty} P\left(\tau_{k}\right) \mathrm{e}^{-k a t} \tag{27}
\end{equation*}
$$

and

$$
\begin{equation*}
\dot{n}=\dot{n}_{0} \sum_{k=1}^{\infty} p\left(\tau_{k}\right) \mathrm{e}^{-k a t} \tag{28}
\end{equation*}
$$

where the summation is over integer-valued $k$. The normalized spectral intensities $P$ and $p$ are given by the following expressions $\left(\sum P=\sum p=1\right)$

$$
\begin{equation*}
P\left(\tau_{k}\right)=\Gamma(1 / \beta+k)\left[\Gamma(1 / \beta) \Gamma(k+1) B^{k}\right]^{-1}\left[(B /(B-1))^{1 / \beta}-1\right]^{-1} \tag{29}
\end{equation*}
$$

and

$$
\begin{equation*}
p\left(\tau_{k}\right)=k P\left(\tau_{k}\right)\left\{1-[(B-1) / B]^{1 / \beta}\right\}(B-1) \beta \tag{30}
\end{equation*}
$$




Figure 8. Discrete distribution of relaxation times for $\dot{n}(t) ; \epsilon=10^{-10}, \beta=6 ; \mathrm{cf}$ equation (30).

Figure 9. Discrete distribution of relaxation times for $\dot{n}(t) ; \epsilon=10^{-2}, \beta=6$; of equation (30).

The discrete structure of the $\tau$ spectra is illustrated in figures $6-9$. Figures 6 and 7 show the distribution $P(\tau)$ for $n(t)$ at $t=0$ for $B=1+10^{-10}$ and $1+10^{-2}$, respectively. Figures 8 and 9 show the corresponding spectra $p(\tau)$ for $\dot{n}(t)$. The value of $\beta$ is 6 in all the diagrams. The intensity of the spectral lines is shown by the vertical full lines. For graphical reasons, lines for $a \tau<0.1$ cannot be included; their intensity follows from the envelope showing the shape of the spectrum.

## 4. Final remarks

The present model can be considered as a generalization of the model described by equation (8) above and discussed earlier [6-8, 11]. The basic idea behind both models is reminiscent of that underlying BE statistics, although in the present case adapted to a time sequence of events believed to mimic the flow of condensed matter. This is expressed by equations (8) and (10), stating that the change in flow rate is proportional to the flow rate times an induction factor linearly dependent on the rate. In other words, this is the well known attraction of objects or events typical of BE statistics. In the present case, however, we do not distribute particles on energy levels, but events along a time scale according to a largely equivalent statistical mechanism, thus producing an $\dot{n}(t)$ dependence typical of such a mechanism.

Basically, the interaction introduced here replaces the $\exp (-a t)$ variation characteristic of independent events with $1 /[B \exp (a t)-1]$, cf equation (11). The parameter $B$ entering the denominator of that equation ensures that divergence is avoided at $t \rightarrow 0$. In conventional quantum statistics the numerator of equations such as (11) for $\dot{n}(t)$ gives the number of cells in the phase space available at a particular energy level. In equations of the present type the situation is similar. While in the simple model presented earlier [ $6-8$ ] this number was constant along the time axis, we now have $a n / \beta$ as the value of the numerator. From a physical point of view, this appears to represent a plausible situation where the events taking place within a given time interval are clustered around a fraction of events taking place spontaneously during the same time interval. Especially interesting is the fact that the value of this fraction is $1 / 6(\beta=6)$, reproducing rather accurately the value of the $F / n_{0}$ ratio found in experiments, equations (4) and (26).

A feature of the present model that should be especially emphasized is its ability to unify in a single formula the characteristics of the exponential and power laws of flow. While retaining a rectilinear portion of the $n(\log t)$ curves from which the inflection slope important for comparison with experiments can be extracted, we also have a long tail at longer times, which can be identified as originating from a power law relating $\dot{n}$ and $n$. In fact, it has been reported that experimental $\sigma(\log t)$ curves exhibit an exponential region in the initial stage of the process, followed by a power law at longer times [10]. For metals, this has been interpreted in terms of a constant density of mobile dislocations during the initial stage, and a density diminishing with time as the process proceeds. The power-law character of equation (14) for $\dot{n}(n)$ is clcarly evident, although in this case this function is a sum of a linear $\dot{n}(n)$ term and a term containing $n \beta$. However, equation (14) can be recast into the form

$$
\begin{equation*}
\dot{n} / n=1 / \beta \tau-\left(1 / t_{\mathrm{i}}\right)\left(n / n_{0}\right)^{\beta} \tag{31}
\end{equation*}
$$

where $\tau=1 / a$, and $t_{i}$ is the inflection time. As discussed above, $t_{i} \ll \tau$. This leads to the approximation

$$
\begin{equation*}
-\dot{n} \simeq\left(1 / t_{i}\right) n^{\beta+1} / n_{0}^{\beta} \tag{32}
\end{equation*}
$$

or

$$
\begin{equation*}
-\dot{n} \simeq A n^{\beta+1} . \tag{33}
\end{equation*}
$$

Consider now the usual expression for a power-law-type stress relaxation, i.e.

$$
\begin{equation*}
-\dot{\sigma}=B\left(\sigma-\sigma_{\infty}\right)^{\nu} \tag{34}
\end{equation*}
$$

where $\sigma_{\infty}$ denotes the stress as $t \rightarrow \infty$ (internal stress). As easily shown, the normalized inflection slope is given by

$$
\begin{equation*}
F /\left(\sigma_{0}-\sigma_{\infty}\right)=\nu^{\nu /(1-\nu)} . \tag{35}
\end{equation*}
$$

Replacing $\nu$ by $\beta+1$ we recover our expression (24) for $F / n_{0}$, thus demonstrating the equivalence of the approximation (24) of our model and the power law. For natural reasons this equivalence applies only to $n(\ln t)$ curves with a negligible $n_{\infty}$
level. When $n_{\infty}$ becomes finite, the final stage of the curves is truncated and does not depict a fully developed power-law process, cf figures $1-3$.

In concluding we note that, for complete relaxation, not only is the value of $\beta \simeq 6$ in agreement with the empirical finding expressed by equation (4), it also fits well into the exponent range found when applying the power law to both stress relaxation and creep. We thus find that the exponents of the power law provide another independent support for the similarity of flow of different solids as expressed by equation (4). It may finally be pointed out that the model presented above allows the power law to be interpreted in a novel fashion starting from a model of unusual simplicity.

## Acknowledgments

The authors would like to express their thanks to Professor W Brostow for valuable discussions. Financial support from the Swedish Board for Technical Development and the Swedish Research Council for Engineering Sciences is gratefully acknowledged.

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